12-1979

Analysis of Mixtures of Chlorine, Chlorine Dioxide and Chlorite

Chu

Follow this and additional works at: https://scholarworks.wmich.edu/masters_theses

Part of the Analytical Chemistry Commons

Recommended Citation

ANALYSIS OF MIXTURES OF CHLORINE, CHLORINE DIOXIDE AND CHLORITE

by

Ying-Chien Chu

A Thesis submitted to the Faculty of The Graduate College of the Degree of Master of Arts

Western Michigan University

Kalamazoo, Michigan December 1979
ACKNOWLEDGEMENT

The author would like to express her thanks to the Western Michigan University Chemistry Department for supplying the necessary instrumentation and laboratory space needed to conduct this research. Also, she is grateful for the financial assistance which they provided. The author also wishes to express her gratitude particularly to Drs. R. Harmon and H. Warren, who have been most helpful in completing this thesis. Also the assistance and encouragement of the rest of the faculty, graduate students, and other staff members of the Chemistry Department is gratefully acknowledged.

Dr. James A. Howell has been an excellent research advisor and teacher. The author is deeply appreciative of his assistance in completing the degree requirements.

A special debt of gratitude is given to Mrs. R. Noyes for her assistance in typing and preparing this thesis.

Ying-Chien Chu
INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is “Missing Page(s)”. If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.

2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in “sectioning” the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.

University Microfilms International
300 N. ZEEB ROAD, ANN ARBOR, MI 48106
18 BEDFORD ROW, LONDON WC1R 4EJ, ENGLAND

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
CHU, YING-CHIEN
ANALYSIS OF MIXTURES OF CHLORINE, CHLORINE DIOXIDE AND CHLORITE.
WESTERN MICHIGAN UNIVERSITY, M.A., 1979
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>PHOTOMETRIC METHODS OF ANALYSIS</td>
<td>2</td>
</tr>
<tr>
<td>CHLORINE</td>
<td>3</td>
</tr>
<tr>
<td>CHLORINE DIOXIDE</td>
<td>4</td>
</tr>
<tr>
<td>CHLORITE</td>
<td>7</td>
</tr>
<tr>
<td>MIXTURES OF CHLORINE, CHLORITE AND CHLORINE DIOXIDE</td>
<td>8</td>
</tr>
<tr>
<td>PROPOSED METHODOLOGY</td>
<td>9</td>
</tr>
<tr>
<td>BACKGROUND</td>
<td>9</td>
</tr>
<tr>
<td>OBJECTIVE</td>
<td>12</td>
</tr>
<tr>
<td>CHLORINE DIOXIDE-CHLORITE MIXTURE</td>
<td>13</td>
</tr>
<tr>
<td>ALDEHYDE-CHLORITE REACTION</td>
<td>13</td>
</tr>
<tr>
<td>APPARATUS</td>
<td>17</td>
</tr>
<tr>
<td>REAGENTS</td>
<td>18</td>
</tr>
<tr>
<td>PROCEDURES</td>
<td>19</td>
</tr>
<tr>
<td>RESULTS</td>
<td>20</td>
</tr>
<tr>
<td>ACID CHROME VIOLET K REACTION</td>
<td>22</td>
</tr>
<tr>
<td>UNKNOWN REAGENT</td>
<td>23</td>
</tr>
</tbody>
</table>

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
<table>
<thead>
<tr>
<th>Topic</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHLORINE DIOXIDE-CHLORINE MIXTURE</td>
<td>24</td>
</tr>
<tr>
<td>CHLORINE-MALONIC ACID REACTION</td>
<td>24</td>
</tr>
<tr>
<td>APPARATUS</td>
<td>24</td>
</tr>
<tr>
<td>REAGENTS</td>
<td>25</td>
</tr>
<tr>
<td>PROCEDURES</td>
<td>26</td>
</tr>
<tr>
<td>RESULTS</td>
<td>31</td>
</tr>
<tr>
<td>RECOMMENDATIONS</td>
<td>34</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>35</td>
</tr>
</tbody>
</table>
INTRODUCTION

Chlorine, chlorine dioxide and chlorite have been widely used throughout industry since the early 1930's. The rapid growth in chlorine consumption in recent years parallels the growth of the organic chemical industries. About sixty-five percent of the chlorine produced in the United States in 1963 was used for the manufacture of organic chemicals such as: solvents, refrigerants, plastics and dyes(1). Chlorine has been used as bleaching reagent in the paper and textile industries also. The bactericidal properties of chlorine have given rise to its use as a disinfectant for treating swimming pools and also municipal water supplies. Chlorine is much too destructive for bleaching wool, silk and other fibers of animal origin. However, chlorine dioxide and chlorite have gained acceptance as a bleaching reagent for these products. Additionally, chlorine dioxide and chlorite have also been used as bleaching and oxidizing agents in other fields such as those industries involved with the manufacture of oil, waxes, fats, and flour. These compounds have also found application in improving the viscosities of rubber-based varnishes and glues as well as in the sterilization of certain foodstuffs.

When used in the purification of water, chlorine
dioxide has often been generated by the action of chlorine on sodium chlorite. Chlorine dioxide offers several advantages over chlorine such as its ability to destroy ill-tasting phenols and to convert iron and manganese rapidly to insoluble salts. In the bleaching of paper pulp, a mixture of both chlorine and sodium chlorite are used. The advantages derived from using such a mixture over chlorine is the improvement of the brightness of the paper pulp accompanied by less destructive action on the cellulosic fibers(2).

Photometric Methods of Analysis

Numerous methods for the determination of chlorine, chlorine dioxide or chlorite have been reported in the literature such as iodometric(3), gravimetric(3), and potentiometric(4). In recent years, photometric methods have become widely accepted, primarily because of their simplicity and specificity.

Chlorine

It has long been recognized that aqueous chlorine solutions undergo disproportionation according to the following reaction:

\[ \text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (I) \]

These solutions have two absorbance maxima in the ultra-
violet region, both of which shift with the changes in pH. When the pH is less than 1.2, the spectrum has a small absorbance maximum in the vicinity of 320 nm and another maximum at about 220 nm. The maximum at 320 nm is due to the combined absorption of chlorine and some hypochlorous acid. When the pH of the solution is increased, a rather well defined maximum is found in the region of 232 to 236 nm. The maximum at 320 nm gradually shifts toward shorter wavelengths until it reaches 292 nm, the absorption maximum of the hypochlorite moiety.

Direct photometric determination of chlorine is complicated by its disproportionation. Nevertheless, there are several very useful indirect photometric methods for the analysis of total chlorine. One of these indirect colorimetric methods uses o-tolidine (o,o'-dimethylbenzidine) as the reagent. o-Tolidine reacts with traces of chlorine to produce an intense yellow colored oxidation product. Chlorine can be quantitated by measuring the intensity of this yellow colored product at 438 nm. However, this method is not specific since other oxidizing agents react with the reagent in the same manner. The color produced depends on the pH of the solution and is most intense when the pH is between 0.8 and 3. At pH 1.6 Beer's law is obeyed at 438 nm in the concentration range of 0 to 1.0 p.p.m. of chlorine. The color intensity reaches a maximum almost immediately and decreases there-
after at a moderate rate. Iron(II), manganese(II) or (IV) and nitrite interfere if present in amounts greater than 0.2, 0.01 and 0.9 p.p.m., respectively. Besides o-tolidine, other methods of indirect photometric analysis of chlorine have used reagents such as methyl orange. The details of these methods can be found in "Colorimetric Determination of Non-metals"(6).

**Chlorine Dioxide**

Colorimetric methods for the determination of chlorine dioxide are well documented(7,8,9). One of the earliest methods was based upon the direct measurement of the ultraviolet absorbance of acidic aqueous solutions of chlorine dioxide at 358 nm. This method is not particularly sensitive since the molar absorptivity of these yellowish solutions is only 1090 \( \text{L mole}^{-1} \text{cm}^{-1} \). Further complicating this method is the tendency of neutral or alkaline chlorine dioxide solutions to undergo a disproportionation reaction.

\[
6\text{ClO}_2 + 3\text{H}_2\text{O} \rightleftharpoons 5\text{ClO}_3^- + \text{Cl}^- + 6\text{H}^+ \quad (\text{II})
\]

This pH dependence of the spectrum of chlorine dioxide has been extensively investigated(10).

Recently several indirect photometric methods for the analysis of chlorine dioxide solutions have been reported. In 1966, Masschelein(11) used acid chrome violet K (1,5-
bis-(4-methylphenylamino-2-sodium sulfonate)-9, 10-anthraquinone) to react with chlorine dioxide. Utilizing the diminution of the absorbance of acid chrome violet K at 550 nm enabled him to successfully determine chlorine dioxide concentrations in aqueous solution. He found that concentrations of active chlorine, and hypochlorite up to 10 p.p.m. gave no interference provided the solutions are buffered between pH of 8.1 and 8.4 and the absorbance was measured within thirty minutes. It was found that two moles of chlorine dioxide react with one mole of acid chrome violet K under these reaction conditions. Iron(II) has also been used as a reagent for the indirect photometric determination of chlorine dioxide solutions(12) by utilizing the following reaction:
\[ \text{ClO}_2 + 5\text{Fe}^{2+} + 4\text{H}^+ \rightleftharpoons \text{Cl}^- + 5\text{Fe}^{3+} + 2\text{H}_2\text{O} \] (III)

By complexing the unreacted excess iron(II) with 1,10-phenanthroline, the tris (1,10-phenanthroline) iron(II) ion is formed. This complex exhibits a maximum absorption at 510 nm with a molar absorptivity of 11,100 \( \text{mol}^{-1} \text{cm}^{-1} \). This indirect procedure takes advantage of the higher molar absorptivity of the complex and the reaction stoichiometry to provide a very sensitive method for chlorine dioxide which has an effective molar absorptivity of 55,500 \( \text{mol}^{-1} \text{cm}^{-1} \). Measurement of the differential absorbance, \( \Delta A \), provides a quantity which is directly proportional to the chlorine dioxide concentration. Sensitivities as low as several p.p.b. can be reasonably expected from this method. The major disadvantage of the method lies in its lack of specificity. Other oxidizing agents such as chlorine, hypochlorite, and chlorite produce serious interferences.

**Chlorite**

In 1953, Friedman(13) investigated the spectrum of the chlorite ion in the ultraviolet region. The chlorite solutions were found to be unstable when acidified as a result of their disproportionation reactions.

\[ 5\text{ClO}_2^- + 4\text{H}^+ \rightleftharpoons 4\text{ClO}_2 + \text{Cl}^- + 2\text{H}_2\text{O} \] (IV)
$8\text{ClO}_2^- + 8\text{H}^+ \leftrightarrow 6\text{ClO}_2 + \text{Cl}_2 + 4\text{H}_2\text{O}$ (V)

The chlorite ion exhibits an absorption maximum at 260 nm with a molar absorptivity between 50 and 800 l mole$^{-1}$cm$^{-1}$ depending upon the pH of the solution. The relatively low molar absorptivity does not readily lend itself to the direct photometric determination of chlorite at p.p.m. levels. Since the chlorite ion was listed as an interference in the indirect method for determining chlorine dioxide with iron(II) and 1,10-phenanthroline(5), it is not surprising to find that this method can also be applied to the determination of the chlorite ion. As a result of the stoichiometry of the chlorite-iron(II) reaction the effective molar absorptivity for the chlorite ion is 44,400 l mole$^{-1}$cm$^{-1}$.

$\text{ClO}_2^- + 4\text{Fe}^{2+} + 4\text{H}^+ \leftrightarrow \text{Cl}^- + 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$ (VI)

Mixtures of Chlorine, Chlorite and Chlorine Dioxide

There are essentially only two compatible mixtures of chlorine, chlorine dioxide and chlorite. One is the mixture of chlorine and chlorine dioxide, while the other is the mixture of chlorine dioxide and chlorite. Since chlorine and chlorite react to form chlorine dioxide, this mixture is not considered to present a significant analytical problem.
2\text{Cl}_2 + \text{Cl}_2 \rightleftharpoons 2\text{ClO}_2 + 2\text{Cl}^-(\text{VII})

Since 1950, a number of studies dealing with the separation of these mixtures by either physical or chemical means have been reported. In 1974, Upatnieks and Cowly(14) used the differences in boiling point and water solubility between chlorine and chlorine dioxide to effect their separation. Jankauskas(15) has reported a titrimetric method for the analysis of chlorine and chlorine dioxide mixtures. This method is limited by an inherent relative error of about eleven percent. Cauquis and Limosin(16) have reported a coulometric method for the analysis of chlorine dioxide and chlorite mixtures. Post and Moore(17) reported that malonic acid can be used to react with chlorine but does not react with chlorine dioxide.

\text{CH}_2(\text{COOH})_2 + \text{Cl}_2 \rightleftharpoons \text{ClCH(OCOO)}_2 + \text{Cl}^- + \text{H}^+ (\text{VIII})

This is a very important finding since it provides a means of differentiating between these two somewhat chemically similar species.

Proposed Methodology

Background

The previously mentioned methods of analysis for mix-
tures of chlorine, chlorine dioxide and chlorite all exhibit difficulties arising from the marked similarity of their chemical and physical properties. These species are all strong oxidizing agents and consequently readily react with most reducing agents. Reagents such as o-tolidine (6) often do not exhibit selective reactivity for these oxidants and therefore are unable to differentiate between the components of their mixtures. Also, special sampling and handling considerations are necessary in order to avoid errors arising from volatility losses of chlorine and chlorine dioxide, both of which exist as gases at room temperature. Furthermore, as a result of their ability to disproportionate, all of these compounds are relatively sensitive to both thermal and photodecomposition (18).

Another difficulty encountered in the analysis of mixtures of chlorine, chlorine dioxide and chlorite arises from the fact that they all exhibit overlapping absorption bands in the ultraviolet region. The maximum absorbance of chlorine can be found between 220 and 240 nm depending upon the pH. Chlorine dioxide exhibits a maximum absorbance at 360 nm, while chlorite exhibits a maximum at 262 nm. The overlapping of these bands presents a strong deterrent to the use of direct absorbance measurements for the analysis of these mixtures.
Chlorine, chlorine dioxide and chlorite all undergo pH dependent disproportionations. Chlorine dioxide slowly disproportionates to form chlorate and chloride. This reaction is shown in equation (II). Therefore, chlorine dioxide solutions should be kept acidic in order to avoid this disproportionation reaction. If the pH of the chlorine dioxide solutions is maintained below 2.5 they are relatively stable. The disproportionation of chlorite is given by equations (IV) and (V). When an excess of acid is present and chlorite concentrations are small, the side reaction shown in equation (V) is not significant. However, if there is an excess of chlorite, the chlorine formed can then react with chlorite to form chlorine dioxide according to the reaction given in equation (VII). Since these reactions occur in acid solution, chlorite solutions should be maintained in a slightly acidic to basic medium. Mixtures of chlorine and chlorine dioxide are stable at pH values less than 2.0. Since chlorine dioxide disproportionates in basic media and chlorite disproportionates in acid media, mixtures of these species exhibit limited stability in a rather narrow range of approximately neutral pH values. Even in these cases, as a result of the disproportionation of chlorite, an equilibrium condition may exist between chlorine dioxide and chlorite as can be seen in equations (IV) and (V).
Objective

Because of these difficulties, the methods previously mentioned are not generally considered satisfactory. The purpose of this investigation was to study various reagents which might selectively react with only one component of the possible chlorine-chlorite-chlorine dioxide mixture. A complete analysis could then be effected by determining the total oxidizing power of the mixture utilizing the iron(II) reaction. The remaining constituents could be determined by difference. Therefore, this investigation can be considered to be comprised of two parts, the first of which is to perform the photometric analysis of mixtures of chlorine dioxide and chlorite, and the other part is to carry out the photometric analysis of chlorine and chlorine dioxide mixtures.
CHLORINE DIOXIDE—CHLORITE MIXTURES

Aldehyde-Chlorite Reaction

In 1941, Jeanes and Isbell(19) found that the aldehyde groups in reducing sugars are oxidized by the chlorite ion to carboxylic acids and chlorine dioxide with negligible side reactions. The fact that the rates of oxidation increase with decreasing pH suggests that chlorous acid is the oxidant. In the presence of an excess of chlorite the net reaction corresponds approximately to the following equation:

\[ RCHO + 3\text{ClO}_2^- + 3\text{H}^+ \rightarrow R\text{COOH} + 2\text{ClO}_2 + \text{HCl} + \text{H}_2\text{O} \]  

(IX)

This reaction is seemingly paradoxical when one considers that the oxidizing agent, chlorous acid, is itself oxidized to form chlorine dioxide. Jeanes and Isbell found that the reaction is complicated by the spontaneous disproportionation of chlorite in acid solution. This can be seen if one considers the reaction shown in equation (IX) to be comprised of two contributing reactions: e.g. the oxidation of the aldehyde by the chlorous acid to form the corresponding acid and chloride ion,

\[ 2RCHO + \text{HClO}_2 \rightleftharpoons 2R\text{COOH} + \text{Cl}^- + \text{H}^+ \]  

(X)
and also by the acid disproportionation of chlorous acid.

\[ 5\text{HClO}_2 \rightleftharpoons 4\text{ClO}_2 + \text{Cl}^- + \text{H}^+ + 2\text{H}_2\text{O} \] (XI)

Consequently in order to observe the reaction stoichiometry indicated in equation (IX), five moles of chlorous acid must disproportionate for every mole of chlorous acid reduced by the aldehyde. Therefore it is hardly surprising to find that acidic solutions of chlorous acid do not exhibit a distinct stoichiometry when reacted with aldehydes. However, Hashini and co-workers(20) have reported that the reaction shown in equation (IX) could be used as the basis for a qualitative test for aldehydes. If one observed the formation of chlorine dioxide, the test was considered positive. The pH of the test solution, however, had to be maintained sufficiently high so as to prevent the formation of chlorine dioxide by the disproportionation of chlorous acid as shown in equation (XI) and thus give a false positive test. The fact that false positive tests can be avoided but yet the aldehyde-chlorous acid reaction can still produce chlorine dioxide causes one to become suspicious of the reaction stoichiometry of equation (IX).

A somewhat speculative, but nevertheless much more plausible, explanation of the observations of Jeanes and Isbell, and Hashini and coworkers can be found if one considers the overall reaction to be comprised of two step-wise reactions. The first of these involves the oxidation
of the aldehyde by chlorous acid to form the carboxylic acid and chlorine.

$$3RCHO + 2HClO_2 \rightleftharpoons 3RCOOH + Cl_2 + H_2O$$ (XII)

The chlorine formed subsequently reacts with excess chlorous acid to produce chlorine dioxide and chloride.

$$Cl_2 + 2HClO_2 \rightleftharpoons 2Cl^- + 2H^+ + 2ClO_2$$ (XIII)

The combination of the reactions given in equations (XII) and (XIII) give an overall reaction with the following stoichiometry:

$$3RCHO + 4HClO_2 \rightleftharpoons 3RCOOH + 2ClO_2 + 2Cl^- + 2H^+ + H_2O$$ (XIV)

Regardless of the stoichiometry of the aldehyde-chlorous acid reaction it is very significant to note that in both studies\(^{(19,20)}\) the chlorine dioxide formed was found to react either very slowly with the aldehyde or not at all. Thus it would appear that since aldehydes tend to readily react with chlorous acid but little or not at all with chlorine dioxide, this reaction might be used to provide a means of differentiating these two species in their mixtures. Thus an analytical procedure could be performed on a mixture of chlorine dioxide and chlorite by first determining the total oxidizing capacity of the solution, and then reacting a portion of the mixture with an appropriate aldehyde, followed again by a determination of the oxidizing capacity.
Therefore, if such an analysis is to be developed, a systematic study of the reaction rates of some aldehydes should be carried out. The first requirement to be imposed on the aldehyde is that it not react significantly with chlorine dioxide. If we assume the following reaction:

\[ 2\text{Cl}_2 + 5\text{RCHO} + \text{H}_2\text{O} \rightleftharpoons 2\text{Cl}^- + 5\text{RCOOH} + 2\text{H}^+ \quad (XV) \]

is a slow reaction and a large excess of aldehyde is maintained, a pseudo-first order reaction will result. Also, the aldehyde must not absorb at the same wavelength as chlorine dioxide, 360 nm. The following equations can be used to determine the half-life of the reaction:

\[
\log A_t = \log A_0 - \frac{k}{2.303} t
\quad (XVI)
\]

and

\[ t_\frac{1}{2} = \frac{0.693}{k} \quad (XVII) \]

where:
- \( A_0 \) = initial absorbance of chlorine dioxide
- \( A_t \) = absorbance of chlorine dioxide at time \( t \)
- \( k \) = pseudo-first order reaction rate constant
- \( t \) = reaction time
- \( t_\frac{1}{2} \) = half-life

**Apparatus**

Reaction rate studies were carried out on a Beckman Instruments Model DB Spectrophotometer at a fixed wavelength of 360 nm. The cell compartment was maintained at
a constant temperature of $28 \pm 0.1^\circ\text{C}$ by means of an E. H. Sargent Co. Thermomonitor and associated water bath, heater and circulator. The analog data were transmitted to an A.R.F. Products, Inc., Model AAM-10 Operational Amplifier for signal conditioning prior to its transmission to a data logging system. The data logging system consisted of a Beckman Instruments Model 3108 Intercoupler and a Teletype Corporation ASR-33 Teletype. The 100% T setting was adjusted on the spectrophotometer and then the operational amplifier "zero" was adjusted until the Teletype printed "100". With the spectrophotometer reading 0.0%T, the "gain" of the operational amplifier was adjusted until the Teletype printed "0000". Reading times were selected by means of the "sample interval" control of the Intercoupler. Usually a sampling rate of one per second was used. The transmittance values were then typed as they were taken. The option of having the data output on the Teletype punched tape was available if desired.

Reagents

Chlorine Dioxide Stock Solution: This solution was prepared and standardized according to the procedure described by Howell, Linington and Boltz(21). Reaction mixtures were prepared by making appropriate dilutions of this stock solution. Standardization was performed daily as required.
Saturated Sodium Acetate Solution: Add 1200 g of anhydrous sodium acetate to 500 ml of distilled water, dilute to 1.0 liter and mix thoroughly to insure saturation.

Acetaldehyde, Propionaldehyde and Benzaldehyde Stock Solutions: Pipette 10, 10 and 30 ml of acetaldehyde, propionaldehyde and benzaldehyde liquids respectively into three separate 100-ml volumetric flasks and dilute to the mark with distilled water. The approximate concentrations of these stock solutions can then be computed from the densities of these liquids at the temperature which the volume measurements were made.

Procedures

Chlorine Dioxide Calibration Plot: A linear calibration plot of chlorine dioxide concentrations from 1.46 p.p.m. to 58.4 p.p.m. was prepared by appropriate dilutions of the chlorine dioxide stock solution and subsequently measuring the absorbance of these solutions at 360 nm vs. a distilled water blank. Typically the slope and intercept of these plots were 0.0161 p.p.m.\(^{-1}\) and 0.001 respectively.

Reaction Rate Mixtures: An appropriate amount of the respective aldehyde stock solution was transferred by pipette to a 100-ml volumetric flask. Then a predetermined amount of standardized chlorine dioxide stock solution was
also transferred to the flask. Immediately an appropriate amount of desired buffer solution was added to bring the solution to the mark. The solution was then mixed thoroughly. An auxiliary timer was started when the chlorine dioxide stock solution was added. A portion of the mixture was then placed in the spectrophotometer and its absorbance monitored at 360 nm as a function of time. Once the "digitizer" was actuated, the auxiliary timer was stopped and its reading recorded.

Results

The procedures mentioned above can provide concentration ratios of aldehyde to chlorine dioxide greater than 20:1. Table I is based on the pseudo-first order reaction equations to calculate the rate constants and half-life of the aldehydes at different pH values. From the data in Table I, none of the aldehydes studied was found to be satisfactory. The principal reason is due to their relatively short half-life. It can be seen that as the pH of the solution increases the half-life decreases. This might be attributed to chlorine dioxide undergoing disproportion to form chlorous acid. It will be recalled that in the reaction of aldehyde with chlorite the oxidant was chlorous acid. If the pH is below 2.0, the half-life of the reaction of chlorine dioxide with aldehydes increases. While the rate of the chlorine dioxide-aldehyde reaction
at low pH values might be sufficiently slow to permit differentiation from the chlorite-aldehyde reaction, the acid disproportionation of chlorite precludes the use of these conditions to effect the analysis of chlorite-chlorine dioxide mixtures. It can be seen from Table I that as the number of carbon atoms in the aldehyde increases, the reaction rate increases. It is not too surprising to find that as the molecular weight of the aliphatic aldehyde increases, the reactivity of the molecule increases. These findings are consistent with the work of Jeanes and Isbell(19), who studied a variety of aldose sugars. Unpublished data from this laboratory has also shown the behavior of aldoses toward chlorine dioxide to be similar to that seen in Table I.

The data for the aromatic aldehyde, benzaldehyde appears promising. It would seem that the reactivity of aromatic aldehydes could be altered favorably by utilizing substituent effects on the ring. Attempts were made to study nitrobenzaldehyde but unfortunately it strongly absorbed ultraviolet region, thus interfering with chlorine dioxide absorbance maximum. The limited water solubility of these compounds necessitated the use of organic solvents. In most cases these solvents tend to be oxidized by chlorine dioxide. In view of the spectral and solubility difficulties associated with aromatic aldehydes, no
further attempts were made to study their reactions with chlorine dioxide.

Table I. Reactions of chlorine dioxide with different aldehydes at different pH values.

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>pH</th>
<th>Concn. of ClO₂ (mM)</th>
<th>RCH0 ClO₂</th>
<th>k'_1 (min⁻¹)</th>
<th>t½ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>3.9</td>
<td>1.25</td>
<td>40:1</td>
<td>0.0119</td>
<td>58.2</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.44</td>
<td>1.55</td>
<td>25:1</td>
<td>0.00784</td>
<td>88.4</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>3.9</td>
<td>1.25</td>
<td>38:1</td>
<td>0.0495</td>
<td>14.0</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>0.46</td>
<td>1.55</td>
<td>23:1</td>
<td>0.0118</td>
<td>52.7</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>0.39</td>
<td>0.84</td>
<td>39:1</td>
<td>0.00691</td>
<td>100.4</td>
</tr>
</tbody>
</table>

k'_1 = pseudo first order rate constant

Acid Chrome Violet K Reaction

Masschelein(11) found that acid chrome violet K reacts with chlorine dioxide without the interference from chlorite. Numerous attempts to purchase this reagent from commercial sources were unsuccessful. Synthesis of acid chrome violet K was considered but subsequently deemed to be beyond the scope of this investigation. Several attempts were made to investigate the reaction of chlorine dioxide with molecules such as 2,6-diaminoanthraquinone and the disodium salt of anthraquinone 2,6-disulfonic acid which possess certain structural similarities to acid chrome violet K. These efforts were not fruitful. Currently, attempts at the synthesis of acid chrom violet K are being made in this department.
Unknown Reagent

A light violet-colored compound which reacts with chlorite to form a yellow solution but not with chlorine dioxide was inadvertently discovered. Unfortunately, the bottle containing this reagent was mislabeled. Attempts to identify the compound have revealed that it is soluble in water and sparingly soluble in methanol. The melting point is above 350°C. Qualitative analysis revealed the presence of sodium, aluminum and oxalate. No proton resonance was found in its NMR spectrum. X-ray powder diffraction studies failed to provide any useful information. The infrared spectrum of this compound revealed a characteristic carbonyl band which is consistent for an oxalate salt. The remaining features of the spectrum were not conclusive. Further efforts to characterize this compound are being carried out by other workers in this laboratory.
CHLORINE DIOXIDE-CHLORINE MIXTURES

Chlorine-Malonic Acid Reaction

Iron(II) may be used to determine the total oxidizing power in a chlorine dioxide-chlorine mixture (21). Malonic acid has been successfully added to remove chlorine interference in chlorine dioxide analyses (17). The reaction is shown in equation (VIII). To one of two identical solutions of chlorine and chlorine dioxide, an excess of malonic acid, sufficient to completely remove any chlorine, was added. Then an equal amount of excess iron(II), followed by 1,10-phenanthroline was added to both solutions. By measuring the differential absorbance of these solutions relative to a reagent blank at 510 nm, one can quantitatively determine the concentrations of chlorine and chlorine dioxide in the original mixtures.

Apparatus

The chlorine dioxide generation apparatus used in this study was similar to that described by Howell and co-workers (21). All absorbance measurements were made with a Cary Model 14 recording spectrophotometer, using 1.00-cm silica cells.

22
Reagents

Iron(II) Ammonium Sulfate Solution: This solution was prepared in accordance with a procedure set forth in the literature(21). It was, however, necessary to substitute 443 mg of Fe(NH$_4$)$_2$(SO$_4$)$_2$•6H$_2$O for 326 mg of Fe(ClO$_4$)$_2$•6H$_2$O called for in the original paper.

Sulfuric Acid Solution: The preparation of this solution was carried out according to the instructions given by Howell, Linington and Boltz(21).

Chlorine Dioxide Stock Solution: The preparation of this solution was described earlier in this thesis on page 16.

Saturated Sodium Acetate Solution: This solution was prepared as described earlier on page 17.

1,10-phenanthroline Solution: The preparation of this solution was in accordance with that reported in the literature(21).

Chlorine Stock Solution: Chlorine gas was vigorously bubbled for about 10 minutes into approximately 400 ml of distilled water which had been cooled to about 4° C. This solution was subsequently standardized iodometrically against a standard sodium thiosulfate solution. The stock solution of chlorine was placed in an amber bottle and kept refrigerated.

Malonic Acid Solution: 5.000 grams of malonic acid was dissolved in 500 ml distilled water.
**Procedures**

Calibration Plot of Tris (1,10-phenanthroline) Iron (II) Ion: A linear calibration plot of the tris (1,10-phenanthroline) iron(II) complex was obtained for concentrations of iron(II) ranging from 0.14 p.p.m. to 6.90 p.p.m. The data were obtained by reacting iron(II) with excess 1,10-phenanthroline buffered to a pH between 3 and 5. The absorbance of these solutions was then measured at 510 nm vs. a distilled water blank. The slope and intercept of this plot was 0.204 p.p.m.\(^{-1}\) and 0.002 respectively.

Calibration Plot of Chlorine Dioxide: Details for this preparation of this plot are given on page 17 of this thesis.

Calibration Plot of Chlorine Dioxide With Excess Iron(II): The procedures described by Howell and co-workers(5) were followed in order to prepare a linear calibration plot for chlorine dioxide concentrations from 28.6 p.p.b. to 286 p.p.b. The slope and intercept of the plot were 0.000846 p.p.b.\(^{-1}\) and 0.002 respectively.

Calibration Plot of Chlorine With Excess Iron(II): 10 ml of 60 p.p.m. iron(II) stock solution was put in a 100-ml volumetric flask which contained 30 ml of 0.6 M sulfuric acid solution. Then an aliquot of chlorine solution containing from 0.3 to 285 \(\mu\)g of the chlorine was added to the flask. The solution was then mixed thoroughly.
and 3 minutes was allowed for the reaction to reach completion. Then 10 ml of 0.1% 1,10-phenanthroline solution and enough saturated sodium acetate solution were added to bring the pH of the solution to between 3 and 5. The solution was then diluted to the mark with distilled water and 10 minutes allowed for complete equilibration to occur. Then the differential absorbance of this solution was measured against a reagent blank at 510 nm. The data obtained from the procedure above gave a linear calibration plot from approximately 0.2 to 3 p.p.m. The slope and intercept of this plot were 0.323 p.p.m.\(^{-1}\) and 0.003 respectively. The data may be seen in Table II.

Table II. Calibration plot data for chlorine with excess iron(II) solution.

<table>
<thead>
<tr>
<th>No. of Detns.</th>
<th>Cl(_2) added (p.p.m.)</th>
<th>Avg. Cl(_2) found (p.p.m.)</th>
<th>Deviation (p.p.m.)</th>
<th>% CV*</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.228</td>
<td>0.149</td>
<td>-0.079</td>
<td>0.4</td>
</tr>
<tr>
<td>9</td>
<td>0.432</td>
<td>0.455</td>
<td>+0.023</td>
<td>2.8</td>
</tr>
<tr>
<td>8</td>
<td>0.913</td>
<td>0.913</td>
<td>0.000</td>
<td>3.4</td>
</tr>
<tr>
<td>9</td>
<td>1.14</td>
<td>1.08</td>
<td>-0.06</td>
<td>0.8</td>
</tr>
<tr>
<td>8</td>
<td>1.58</td>
<td>1.69</td>
<td>-0.11</td>
<td>1.7</td>
</tr>
<tr>
<td>9</td>
<td>2.28</td>
<td>2.15</td>
<td>-0.13</td>
<td>1.5</td>
</tr>
<tr>
<td>8</td>
<td>2.85</td>
<td>2.69</td>
<td>-0.16</td>
<td>0.7</td>
</tr>
</tbody>
</table>

*CV = coefficient of variation

Determination of Chlorine and Chlorine Dioxide in Mixtures: 5 ml of 1% malonic acid was added to one of two 100-ml volumetric flasks. Then equal aliquots of the
chlorine–chlorine dioxide mixture were added to both flasks. Both flasks were stoppered and the one which contained malonic acid was thoroughly mixed. Five minutes were allowed to permit the chlorine to react completely. Then 15 ml of 3 M sulfuric acid and 10 ml of 60 p.p.m. iron(II) solution was added to both volumetric flasks. After 20 minutes, 10 ml of 0.1% 1,10-phenanthroline and enough saturated sodium acetate solution to buffer to a pH of 3 to 5 was added. Both solutions were then diluted to the mark with distilled water. After 10 minutes to permit equilibration, the differential absorbance vs. a reagent blank at 510 nm was measured for both solutions. The difference in the differential absorbance values can be used to determine the chlorine content from the chlorine calibration plot. The concentration of chlorine dioxide can be found from the differential absorbance of the solution containing malonic acid and the calibration plot for chlorine dioxide with excess iron(II). Typical analysis data for this method is shown in Table III.
Table III. Determination of mixtures of chlorine and chlorine dioxide with excess iron(II) solution.

<table>
<thead>
<tr>
<th>No. of Detns.</th>
<th>Added $\text{Cl}_2$ (p.p.b.)</th>
<th>$\text{Cl}_2$ (p.p.m.)</th>
<th>Av. Found $\text{Cl}_2$ (p.p.b.)</th>
<th>$\text{Cl}_2$ (p.p.m.)</th>
<th>Deviation $\text{Cl}_2$ (p.p.b.)</th>
<th>Deviation $\text{Cl}_2$ (p.p.m.)</th>
<th>Coef. of Var. $\text{Cl}_2$ (%)</th>
<th>Coef. of Var. $\text{Cl}_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>22.4</td>
<td>0.91</td>
<td>22.4</td>
<td>0.895</td>
<td>0</td>
<td>-0.015</td>
<td>1.8</td>
<td>3.2</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>2.3</td>
<td>38</td>
<td>2.04</td>
<td>+2</td>
<td>-0.26</td>
<td>0.7</td>
<td>2.1</td>
</tr>
<tr>
<td>8</td>
<td>119</td>
<td>1.47</td>
<td>129</td>
<td>1.37</td>
<td>+10</td>
<td>-0.1</td>
<td>2.3</td>
<td>4.2</td>
</tr>
<tr>
<td>8</td>
<td>271</td>
<td>0.787</td>
<td>265</td>
<td>0.763</td>
<td>-6</td>
<td>-0.024</td>
<td>1.6</td>
<td>3.7</td>
</tr>
<tr>
<td>8</td>
<td>370</td>
<td>2.13</td>
<td>350</td>
<td>1.94</td>
<td>-20</td>
<td>-0.19</td>
<td>3.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Results

The reaction of an equimolar chlorine-chlorine dioxide mixture with excess iron(II) involves the oxidation of seven equivalents of iron(II). This reaction is shown below:

\[ \text{Cl}_2 + \text{ClO}_2 + 7\text{Fe}^{2+} + 4\text{H}^+ \rightleftharpoons 3\text{Cl}^- + 7\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad \text{(XVIII)} \]

The relatively large molar change of iron and the high molar absorptivity of tris (1,10-phenanthroline) iron(II) complex gives this indirect spectrophotometric method very good sensitivity. In addition, this reaction was found to be rapid and stoichiometric when carried out in the solutions of sulfuric acid which were 0.5 M or greater. Nevertheless, a number of factors will influence the results.

According to the kinetic studies of chlorine with malonic acid it was found that the reaction was complete within 5 minutes. If the time was less than 5 minutes, chlorine may not be eliminated completely. This then causes lower results for chlorine and higher results for chlorine dioxide. On the other hand the total time elapsed before iron(II) is added to the mixture should not exceed 30 minutes, or a serious volatility problem results.

Provided the concentration of chlorine and chlorine dioxide does not exceed the microequivalents of iron(II) the system adheres to Beer's Law. Concentrations greater
than this require larger quantities of reagents and correspondingly longer reaction times.

The reaction of chlorine and chlorine dioxide was not found to be critical, provided the hydrogen ion concentration was in excess of 0.5 M. Lower concentrations of acid causes the reaction to become very slow. Too large of an excess of hydrogen ion can cause a problem since an excessively large amount of saturated sodium acetate will be needed to bring the pH between 3 and 5. Improper pH adjustment seriously interferes with the color development of the tris (1,10-phenanthroline) iron(II) complex.

Iron(II) should not be in too large of an excess after reaction or else the color intensity may be too great for the spectrophotometer to accommodate in the reference beam. Also associated with the high iron(II) concentrations after reaction, are wide slits, thus increasing the possibility of errors arising from the finite slit width effect. In this investigation it was found desirable to maintain excess iron(II) concentrations to less than 6 p.p.m.

Precision: From the data which is shown in Table III, one finds that there are two factors which influence the precision of the method. One is the high degree of volatility of chlorine and chlorine dioxide, as evidenced by the trend toward negative deviations. The other factor arises from the instability of these two compounds. Pro-
vided that the analysis time is kept short this latter factor may not exert much influence on the results. However, improved solution transfer techniques should tend to minimize these errors.

Interferences: A study of interferences for the chlorine dioxide determination have been reported by Howell and co-workers (21). It is reasonable to expect these interferences to play a similar role in the analysis of chlorine by this method. Results of an additional study of interferences for the chlorine method are shown in Table IV.

An interference was determined to exist at a given concentration if its addition to a mixture of 100 p.p.b. of each chlorine and chlorine dioxide results in a relative error in either determination greater than 2.5%. The precise nature of an interference was not investigated in this study.

Table IV. Interference of diverse ions on the determination of mixtures of chlorine and chlorine dioxide.

<table>
<thead>
<tr>
<th>Ion Added</th>
<th>Conc. of Ion (p.p.m.)</th>
<th>% Relative Error</th>
<th>Permissible Amount (p.p.m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>500</td>
<td>+0.8</td>
<td>500</td>
</tr>
<tr>
<td>K⁺</td>
<td>500</td>
<td>+0.4</td>
<td>500</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>500</td>
<td>+1.5</td>
<td>500</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>10</td>
<td>+7</td>
<td>1</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>100</td>
<td>+2</td>
<td>200</td>
</tr>
<tr>
<td>ClO₃⁻</td>
<td>50</td>
<td>+5</td>
<td>10</td>
</tr>
<tr>
<td>SiO₃²⁻</td>
<td>0.2</td>
<td>-14</td>
<td>0.1</td>
</tr>
</tbody>
</table>
RECOMMENDATIONS

The indirect spectrophotometric analysis of the mixtures of chlorine and chlorine dioxide using the iron(II) reaction has been shown to be a rapid, simple and sensitive method.

If acid chrome violet K can be obtained, this method can be equally applicable to the analysis of mixtures of chlorine dioxide and chlorite. Further refinement of the techniques developed in this study should be carried out for the purpose of minimizing the volatility problems encountered with these compounds.
REFERENCES


VITA

The author of this paper was born October 30, 1951 in Taipei, Taiwan. She graduated from Chung-Shan Girls' High School in 1970. She passed the National Universities' Entrance Examination and then became a student of Chung-Yuan Christian College of Science and Engineering. She graduated with a B.S. in Chemistry in 1974. She got the teaching assistantship from the Chemistry Department of Western Michigan University in 1975. She is currently a member of the Water and Waste Water Analyst Association.